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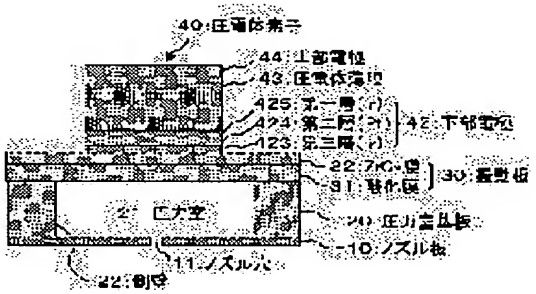
(54) PIEZOELECTRIC ELEMENT, MANUFACTURING METHOD THEREFOR, INK JET RECORDING HEAD, AND PRINTER

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a piezoelectrics element having stable high piezoelectric characteristics, an ink jet recording head, and a printer.
SOLUTION: There are sequentially laminated a lower electrode 42 (a third layer 423 comprising Ir, a second layer 424 comprising Pt, and a first layer 425 comprising Ir), a Ti layer of 4-6 nm, a piezoelectrics thin film 43, and an upper electrode 44, on a ZrO2 film 32. A 100 plane orientation degree of the piezoelectrics 43 measured by an X-ray diffraction wide angle method is 40-70%, a 110 plane orientation degree of it 10% or less, and a remaining 111 plane orientation degree. Here, the thickness of the lower electrode second layer 424 is 30-50% of the entire thickness of lower electrode 42.



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CLAIMS

[Claim(s)]
[Claim 1] It is the piezo electric crystal component to which it is the piezo electric crystal component equipped with the lower electrode formed on ZrO2 film, the piezo electric crystal film formed on this lower electrode, and the up electrode formed on this piezo electric crystal film, and is characterized by the 100th page amount of preferred orientation which measured said piezo electric crystal film by the X diffraction wide angle method being 70% or less 40% or more.
[Claim 2] It is the piezo electric crystal component which is a piezo electric crystal component according to claim 1, and is characterized by for the 110th page amount of preferred orientation which measured said piezo electric crystal film by the X diffraction wide angle method being 10% or less, and the 111st page amount of preferred orientation being the remainder.
[Claim 3] It is a piezo electric crystal component according to claim 1. Said lower electrode It has at least the first pass which is located in the maximum upper layer and contains Ir, and the second layer which is located in the following layer and contains Pt. and — this — the piezo electric crystal component characterized by for the thickness of the second layer being 50% or less, having formed with a 4nm or more thickness [6nm or less] Ti layer on said lower electrode 30% or more to the thickness of the whole lower electrode, and forming the piezo electric crystal film on this Ti layer.
[Claim 4] It is the piezo electric crystal component characterized by being a piezo electric crystal component according to claim 3, and equipping said lower electrode with the third layer which is said layer [second] following layer, is located in the lowest layer of said lower electrode, and contains Ir.
[Claim 5] The piezo electric crystal component characterized by being a piezo electric crystal component according to claim 3, and said second layer which contains Pt among said lower electrodes being the lowest layer.
[Claim 6] It is a piezo electric crystal component according to claim 1. Said lower electrode It has at least the first pass which is located in the maximum upper layer and contains Pt, and the second layer which is located in the following layer and contains Ir. And the piezo electric crystal component characterized by for the thickness of this first pass being 40% or less, having formed with a 4nm or more thickness [6nm or less] Ti layer on said lower electrode 20% or more to the thickness of the whole lower electrode, and forming the piezo electric crystal film on this Ti layer.
[Claim 7] The piezo electric crystal component characterized by being a piezo electric crystal component according to claim 6, and said second layer which contains Ir among said lower electrodes being the lowest layer.
[Claim 8] The ink jet type recording head characterized by preparing the piezo electric crystal component according to claim 1 to 7 as an electrostrictive actuator on the diaphragm which is the installation side of this piezo electric crystal component.
[Claim 9] The printer characterized by having the ink jet type recording head according to claim 8 as a printing means.
[Claim 10] The process which forms ZrO2 film on a substrate, and the process which forms a lower electrode on this ZrO2 film, The process which forms with a 4nm or more thickness [6nm or less] Ti layer on this lower electrode, It is the manufacture approach of a piezo electric crystal

component equipped with the process which forms the piezo electric crystal precursor film on this Ti layer, and a baking process. Said lower electrode It has at least the first pass which is located in the maximum upper layer and contains Ir, and the second layer which is located in the following layer and contains Pt. and — this — the process in which the thickness of the second layer is 50% or less, and forms said lower electrode 30% or more to the thickness of the whole lower electrode The manufacture approach of the piezo electric crystal component characterized by what it has for the process which forms said second layer containing Pt, and the process which forms said first pass containing Ir on this second layer at least.

[Claim 11] The process which forms ZrO2 film on a substrate, and the process which forms a lower electrode on this ZrO2 film, The process which forms with a 4nm or more thickness [6nm or less] Ti layer on this lower electrode, It is the manufacture approach of a piezo electric crystal component equipped with the process which forms the piezo electric crystal precursor film on this Ti layer, and a baking process. Said lower electrode It has at least the first pass which is located in the maximum upper layer and contains Pt, and the second layer which is located in the following layer and contains Ir. And the process in which the thickness of this first pass is 40% or less, and forms said lower electrode 20% or more to the thickness of the whole lower electrode The manufacture approach of the piezo electric crystal component characterized by what it has for the process which forms said second layer containing Ir, and the process which forms said first pass containing Pt on this second layer at least.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] When this invention relates to the piezo electric crystal component which has an electric machine conversion function and is especially used for an ink jet type recording head, it relates to the manufacture approach of the piezo electric crystal component from which the outstanding piezo-electric property is acquired, an ink jet type recording head, a printer, and a piezo electric crystal component.
[0002]
[Description of the Prior Art] A piezo electric crystal component is used for an ink jet type recording head as a driving source of the ink regurgitation of a printer. Generally this piezo electric crystal component is equipped with a piezo electric crystal thin film, the up electrode arranged on both sides of this, and a lower electrode, and is constituted.
[0003] The piezo electric crystal component which aimed at the property improvement is developed by specifying conventionally the crystal structure of the thin film which consists of PZT (PZT), or making Ti nucleus form on a lower electrode. For example, the PZT thin film which equipped JP,10-81016,A with the crystal structure of a rhombohedral system, and equipped it with the predetermined amount of preferred orientation is indicated. Moreover, the piezo electric crystal component in which the titanium nucleus was formed on the lower electrode of Ir is indicated by JP,8-335676,A.
[0004] However, with the conventional piezo electric crystal component, there was a problem that it was difficult to be stabilized and to obtain the predetermined amount of preferred orientation of a piezo electric crystal thin film with sufficient repeatability. It is difficult for such a piezo electric crystal component to acquire the stable piezo-electric high property, and it has become the factor which cannot fully obtain an ink jet type recording head or the printing engine performance of a printer.
[0005]
[Problem(s) to be Solved by the Invention] The object of this invention is by canceling the above-mentioned trouble, being stabilized and obtaining the predetermined amount of preferred orientation of a piezo electric crystal thin film with sufficient repeatability to provide the ink JIETO type recording head using a piezo electric crystal component and this equipped with the stable piezo-electric high property, and a printer list with the manufacture approach of a piezo electric crystal component.
[0006]
[Means for Solving the Problem] The piezo electric crystal component of this invention is a piezo electric crystal component equipped with the lower electrode formed on ZrO2 film, the piezo electric crystal film formed on this lower electrode, and the up electrode formed on this piezo electric crystal film, and the 100th page amount of preferred orientation which measured said piezo electric crystal film by the X diffraction wide angle method is characterized by being 70% or less 40% or more.
[0007] Moreover, it is desirable that the 110th page amount of preferred orientation is 10% or less, and the 111st page amount of preferred orientation is the remainder.

[0008] the first pass which said especially lower electrode is located in ** maximum upper layer, and contains Ir, and the second layer which is located in the following layer and contains Pt — at least — having — and — this — to the thickness of the whole lower electrode, the thickness of the second layer is 50% or less, forms with a 4nm or more thickness [6nm or less] Ti layer on said lower electrode 30% or more, and forms the piezo electric crystal film on this Ti layer. **-1 [moreover,] — the third layer which is said layer [second] following layer, is located in the lowest layer of said lower electrode, and contains Ir — having — **** — **-2 — said second layer which contains Pt among said lower electrodes may be the lowest layer.
[0009] Moreover, said lower electrode is equipped with the first pass which is located in ** maximum upper layer and contains Pt, and the second layer which is located in the following layer and contains Ir at least. And it is characterized by for the thickness of this first pass being 40% or less, having formed the layer of with a 4nm or more thickness [6nm or less] Ti nucleus on said lower electrode 20% or more, to the thickness of the whole lower electrode, and forming the piezo electric crystal film on this Ti layer. **-1 [moreover,] — said second layer which contains Ir among said lower electrodes may be the lowest layer.
[0010] Moreover, this invention is an ink jet type recording head characterized by being prepared as an electrostrictive actuator on the diaphragm whose above-mentioned piezo electric crystal component is an installation side.
[0011] Moreover, this invention is a printer characterized by having this ink jet type recording head as a printing means.
[0012] Furthermore, the process at which this invention forms ZrO2 film on a substrate and the process which forms a lower electrode on this ZrO2 film, The process which forms the layer of with a 4nm or more thickness [6nm or less] Ti nucleus on this lower electrode, It is the manufacture approach of a piezo electric crystal component equipped with the process which forms the piezo electric crystal precursor film on this Ti layer, and a baking process. The ** aforementioned lower electrode It has at least the first pass which is located in the maximum upper layer and contains Ir, and the second layer which is located in the following layer and contains Pt. and — this — the process in which the thickness of the second layer is 50% or less, and forms said lower electrode 30% or more to the thickness of the whole lower electrode [whether it has at least the process which forms said second layer containing Pt, and the process which forms said first pass containing Ir on this second layer, and] Or the ** aforementioned lower electrode is equipped with the first pass which is located in the maximum upper layer and contains Pt, and the second layer which is located in the following layer and contains Ir at least. And it is characterized by equipping the thickness of this first pass with the process which forms said second layer in which the process which is 40% or less and forms said lower electrode 20% or more to the thickness of the whole lower electrode contains Ir, and the process which forms said first pass containing Pt on this second layer at least.
[0013]
[Embodiment of the Invention] (Principle explanation) Drawing which measured the relation between the 100th page amount of preferred orientation of a piezo electric crystal thin film and the thickness of Ti nucleus is shown about the piezo electric crystal component which formed the lower electrode by which the laminating was carried out in the order of Ir layer / Pt layer / Ir layer, and Ti nucleus on ZrO2 film, formed the piezo electric crystal precursor film in drawing 9 further, and it was made to crystallize. In <A HREF="/Tokujitu/tjitemdrw.ipdl?N0000=239&N0500=1E_N/;<=8;;8=///&N0001=49&N0552=9&N0553=000011" TARGET="tjitemdrw">> drawing 9, the thickness of the second layer of the lower electrode with which sign (a) contains Pt shows about 10% of case to the thickness of the whole lower electrode. In this case, the thickness of Ti nucleus is able to raise the 100th page amount of preferred orientation to about 90% in 4nm or more 6nm or less. However, when it is going to adjust the 100th page amount of preferred orientation to a different value from this, it is too large, and fluctuation of the 100th page amount of preferred orientation to change of the thickness of Ti nucleus is stabilized, and cannot obtain the desired 100th page amount of preferred orientation with sufficient repeatability.
[0014] On the other hand, sign (b) of drawing 9 shows the case where the ratio to the thickness of the whole lower electrode of the thickness of the second layer of the lower electrode containing Pt

is made to increase from the case of the above-mentioned (a). In this case, in response to the effect of Pt, the 111st page amount of preferred orientation of a piezo electric crystal thin film goes up, and while becoming lower than the case where the 100th page amount of preferred orientation is the above-mentioned (a), the value in which the thickness of Ti nucleus was stabilized by the 100th page amount of preferred orientation in 4nm or more 6nm or less is shown.
[0015] Thus, while setting thickness of Ti nucleus to 4-6nm, it becomes possible by adjusting the rate of the thickness of Pt layer to the thickness of the whole lower electrode to double with repeatability sufficient in proportion of a request of the 100th page amount of preferred orientation (ratio of the 100th page amount of preferred orientation and the 111st page amount of preferred orientation).
[0016] Hereafter, the gestalt of suitable operation of this invention is explained, referring to a drawing.
[0017] (Operation gestalt 1) Drawing 1 is layer structure section drawing which expanded the piezo electric crystal component part of the ink jet type recording head in this operation gestalt.
[0018] As shown in drawing 1 , on the oxide film 31, the piezo electric crystal component 40 carries out the laminating of ZrO2 film 32, the lower electrode 42, the piezo electric crystal thin film 43, and the up electrode 44 one by one, and is constituted.
[0019] An oxide film 31 is formed for example, on the pressure room substrate 20 which consists of single crystal silicon with a thickness of 220 micrometers. Suitably, the film which consists of silicon oxide (SiO2) is formed and obtained in thickness of 1.0 micrometers.
[0020] ZrO2 film 32 is a layer equipped with elasticity, and constitutes the diaphragm 30 united with an oxide film 31. In order to equip this ZrO2 film 32 with the function to give elasticity, it has 200nm or more thickness of 800nm or less preferably.
[0021] Between ZrO2 film 32 and the lower electrode 42, a metal which sticks both layers, and the adhesion layer (not shown) which consists of titanium or chromium preferably may be prepared. An adhesion layer is formed in order that the adhesion to the installation side of a piezo electric crystal component may improve, and when the adhesion concerned can be secured, it is not necessary to form it. Moreover, since when preparing an adhesion layer enables it to secure minimum adhesion, preferably considers as the thickness of 10nm or more.
[0022] The third layer, to 423 and the thickness of the lower electrode 42, it is 30% or more 50% or less of thickness, and the lower electrode 42 consists of 424 and the first passes 425 which are located in the maximum upper layer and contain Ir containing Pt for which are located in the lowest layer and Ir is included the second layer. Especially a limit does not have the thickness of the whole lower electrode 42, for example, it sets it to 100nm. In addition, it is desirable that the relation of dT=3.6xd0+2.4xd1+0.8xd2+2.3xd3 is filled in the thickness of the adhesion layer before baking when the third layer of the thickness of the whole lower electrode after d3 and baking is set [the thickness of 423 / d1 and the thickness of the second layer] to dT for the thickness of d2 and the first pass, d0 and.
[0023] The layer (not shown) of Ti nucleus is formed on the lower electrode 42. Ti nucleus is 6nm or less in 4nm or more thickness.
[0024] The piezo electric crystal thin film 43 is the ferroelectric which consisted of crystals of usual piezoelectric ceramics, and consists of ferroelectricity piezoelectric ingredients, such as titanic-acid lead zirconate (PZT), and a thing which added metallic oxides, such as niobium oxide, nickel oxide, or a magnesium oxide, to this preferably. The presentation of the piezo electric crystal thin film 43 is suitably chosen in consideration of the property of a piezo electric crystal component, an application, etc. Specifically, lead titanate (PbTiO3), titanic-acid lead zirconate (Pb (Zr, Ti) O3), zirconic acid lead (PbZrO3), a lead titanate lanthanum (Pb, La) (TiO3), the PZT lanthanum (Pb, La) (Zr, Ti) (O3), or magnesium niobic acid zirconium lead titanate (Pb(Zr, Ti) (Mg, Nb) O3) is used suitably. Moreover, the film excellent in the piezo-electric property can be obtained by adding niobium (Nb) suitably in lead titanate or zirconic acid lead.
[0025] The 100th page amount of preferred orientation which measured the piezo electric crystal thin film 43 by the X diffraction wide angle method is 70% or less 40% or more. And the 111st page amount of preferred orientation of the 110th page amount of preferred orientation is the remainder 10% or less.

[0026] It is necessary to hold down the thickness of the piezo electric crystal thin film 43 to extent which a crack does not generate in a production process, and to make it thick to extent which presents sufficient displacement property on the other hand for example, and it is set to 1500nm.
[0027] The up electrode 44 is an electrode which becomes the lower electrode 42 and a pair, and is suitably constituted by Pt or Ir. The thickness of the up electrode 44 is about 50nm suitably.
[0028] Drawing 4 is the perspective view part sectional view showing the structure of the body of the ink jet type recording head of this invention.
[0029] As shown in drawing 4 , an ink jet type record head consists of a nozzle plate 10, a pressure room substrate 20, a diaphragm 30, and a piezo electric crystal component 40.
[0030] The pressure room substrate 20 is equipped with the pressure room (cavity) 21, the side attachment wall 22, the reservoir 23, and the feed hopper 24. The pressure room 21 is formed as space stored in order to carry out the regurgitation of the ink etc. by etching substrates, such as silicon. The side attachment wall 22 is formed so that the pressure room 21 may be divided. The reservoir 23 serves as passage for filling ink in each pressure room 21 in common. The feed hopper 24 is formed in each pressure room 21 possible [installation of ink] from the reservoir 23.
[0031] A nozzle plate 10 is stuck on one field of the pressure room substrate 20 so that the nozzle 11 may be arranged in the location corresponding to each of the pressure room 21 established in the pressure room substrate 20.
[0032] The laminating of an oxide film 31 and the ZrO2 film 32 is carried out, and a diaphragm 30 is formed, as mentioned above. The piezo electric crystal component 40 of this invention is formed as an electrostrictive actuator on the diaphragm 30 concerned. The piezo electric crystal component 40 equipped with the layer system shown in drawing 1 , respectively is formed in the location on the diaphragm 30 corresponding to each pressure room 21. The ink tank opening 35 is formed in a diaphragm 30, and supply to the pressure room substrate 20 interior of it is attained at it in the ink stored in the ink tank which is not illustrated.
[0033] The pressure room substrate 20 with which the nozzle plate 10 and the diaphragm 30 were formed is stored in the case which is not illustrated further, and constitutes the ink jet type recording head.
[0034] In the above-mentioned configuration, if an electrical potential difference is impressed between the lower electrode 42 of the piezo electric crystal component 40, and the up electrode 44 and the piezo electric crystal component 40 is distorted, a diaphragm 30 will deform corresponding to the distortion. A pressure is applied to the ink in the pressure room 21 according to the deformation, and the drop of ink carries out the regurgitation from a nozzle 11.
[0035] The perspective view which explains the structure of the printer 100 of this operation gestalt to drawing 5 is shown. As shown in drawing 5 , as for the printer 100, the ink jet type recording head 1, the tray 3, the exhaust port 4, the feed device 6, the control circuit 8, and control-panel 9 grade of this invention which is a printing means are prepared in the body 2 of a printer.
[0036] The tray 3 is constituted by the feed device 6 possible [supply] in the form 5 before printing. A control circuit 8 outputs the printing signal Sh which makes the feed signal Sd which makes a form 5 convey in the feed device 6, and printing perform to the ink jet type recording head 1 based on the printing information supplied from the control or the outside from a control panel 9. The feed device 6 consists of motor 600 grades which drive the rollers 601 and 602 and them which incorporate a form 5, and it is possible to incorporate a form 5 in a body 2 based on the feed signal Sd. If the ink jet type recording head 1 crosses the form 5 top supplied by the feed device 6, and is constituted movable and the printing signal Sh is supplied from a control circuit 8, when the piezo electric crystal component 40 deforms, it is possible to breathe out ink and to print on a form 5. The exhaust port 4 is the outlet which can discharge the form 5 which printing ended.
[0037] (Operation gestalt 2) Drawing 2 is layer structure section drawing which expanded the piezo electric crystal component part of the ink jet type recording head in the 2nd operation gestalt of this invention.
[0038] With this operation gestalt, the lower electrode 42 is 30% or more 50% or less of thickness to the thickness of the lower electrode 42, and the point which consists of 426 and the first

passes (the maximum upper layer) 427 containing Ir containing Pt the second layer (the lowest layer) differs from the above-mentioned operation gestalt 1.
[0039] (Operation gestalt 3) Drawing 3 is layer structure section drawing which expanded the piezo electric crystal component part of the ink jet type recording head in the 3rd operation gestalt of this invention.
[0040] With this operation gestalt, to 428 and the thickness of the lower electrode 42, it is 20% or more 40% or less of thickness, and the second layer (the lowest layer) of the point which consists of the first passes (the maximum upper layer) 429 containing Pt for which the lower electrode 42 contains Ir differs from the above-mentioned operation gestalt 1.
[0041] (The manufacture approach) Next, the manufacture approach of the piezo electric crystal component of this invention is explained. Drawing 6 and drawing 7 are the cross sections showing the manufacture approach of the piezo electric crystal component of this invention, and an ink jet type recording head.
[0042] an oxide-film formation process (S1) — this process is a process which forms the oxide film 31 which carries out high temperature processing in the oxidizing atmosphere containing oxygen or a steam, and consists of oxidation silicon (SiO2). A CVD method besides the usually used oxidizing [thermally] method can also be used for this process.
[0043] It is the process which forms ZrO2 film 32 on the oxide film 31 on the process (S2) pressure room substrate 20 which forms ZrO2 film. This ZrO2 film 32 carries out high temperature processing of what formed the layer of Zr with the spatter or the vacuum deposition method in an oxygen ambient atmosphere, and is obtained.
[0044] If it is in the lower electrode concerning the process (S3) operation gestalt 1 which forms a lower electrode It consists of the process which contains Ir on ZrO2 film 32 and which forms 423 [layer / third], a process which is 30% or more 50% or less of thickness to the thickness of the lower electrode 42 on this third layer, and contains Pt and which forms 424 [layer / second], and a process which forms the first pass 425 containing Ir on this second layer.
[0045] If it is in the lower electrode concerning the operation gestalt 2, on ZrO2 film 32, to the thickness of the lower electrode 42, it is 30% or more 50% or less of thickness, and consists of a process containing Pt which forms 426 [layer / second], and a process which forms the first pass 424 containing Ir on this second layer.
[0046] If it is in the lower electrode concerning the operation gestalt 3, it consists of a process which contains Ir on ZrO2 film 32 and which forms 428 [layer / second], and a process which forms the first pass 429 which is 20% or more 40% or less of thickness, and contains Pt to the thickness of the lower electrode 42 on this second layer.
[0047] On ZrO2 film 32, each class 423-429 makes Ir or Pt adhere in a spatter etc., and forms it, respectively. In addition, in advance of formation of the lower electrode 42, the adhesion layer (not shown) which consists of titanium or chromium may be formed with a spatter or a vacuum deposition method.
[0048] This process is a process which forms a titanium crystal (not shown) in the shape of an island on the lower electrode 42 by a spatter etc. like ** which forms Ti nucleus (layer). By growing up PZT by using a titanium crystal as a nucleus, crystal growth happens from a lower electrode side, and forming Ti nucleus (layer) has it, and it is because a column-like crystal is obtained.
[precise]
[0049] the process (S4) which forms the piezo electric crystal precursor film — this process is a process which forms piezo electric crystal precursor film 43' with a sol-gel method.
[0050] First, the sol which consists of an organic metal alkoxide solution is applied on Ti nucleus by the applying methods, such as a spin coat. Subsequently, fixed time amount desiccation is carried out with constant temperature, and a solvent is evaporated. After desiccation, fixed time amount cleaning is further carried out at a predetermined elevated temperature under an atmospheric-air ambient atmosphere, and the pyrolysis of the organic ligand configurated to the metal is carried out, and it considers as a metallic oxide. Each process of this spreading, desiccation, and cleaning is repeated 4 times or more the number of predetermined times, for example, and the laminating of the piezo electric crystal precursor film of four or more layers is carried out. By these desiccation and cleaning processings, the metal alkoxide and acetate in a solution form the network of a metal,

oxygen, and a metal through the pyrolysis of a ligand.
[0051] It is the process which it calcinates [process] and crystallizes the piezo electric crystal precursor film after formation of baking process (S5) piezo electric crystal precursor film 43'. By this baking, piezo electric crystal precursor film 43' changes to the thin film in which the perovskite crystal structure is formed in from the precursor of an amorphous condition, and an electric machine conversion operation is shown, and the 100th page amount of preferred orientation measured by the X diffraction wide angle method serves as 70% or less of piezo electric crystal thin film 40% or more.
[0052] The up electrode 44 is formed by electron beam vacuum deposition or the spatter on the piezo electric crystal thin film 43 at the up electrode formation process (S6) last.
[0053] If it etches and operates orthopedically in the configuration of having been suitable for the activity part and the piezoelectric component 40 obtained at the above process is manufactured possible [impression of an electrical potential difference] to vertical inter-electrode one, it is possible to make it operate as a piezo electric crystal component of this invention.
[0054] The obtained piezoelectric component 40 is etched so that an ink jet type recording head may be suited, and it is explained below about the process fabricated in the configuration as a piezo electric crystal component based on drawing 7 .
[0055] a piezo electric crystal component forming cycle (S7) — the mask of the piezo electric crystal component 40 is first carried out to the configuration fitted to each pressure room 21, and the perimeter is etched. Specifically, the resist ingredient of uniform thickness is first applied on an up electrode using approaches, such as the spinner method and a spray method. Subsequently, after forming a mask in the configuration of a piezo electric crystal component, exposure and development of are done, and a resist pattern is formed on the up electrode 44. Ion milling or the dry etching method usually used for this is applied, etching clearance of the up electrode 44, the piezo electric crystal thin film 43, and the lower electrode 42 is carried out, and each piezo electric crystal component 40 is fabricated.
[0056] Anisotropic etching which used activity gases, such as anisotropic etching or parallel plate mold reactive ion etching, is performed to the field of another side of a pressure room formation process (S8), next the pressure room substrate 20 with which the piezo electric crystal component 40 was formed, and the pressure room 21 is formed in it. The part left behind without being etched becomes a side attachment wall 22.
[0057] A nozzle plate 10 is stuck on the pressure room substrate 20 after etching with adhesives at the nozzle plate lamination process (S9) last. the time of lamination — each nozzle 11 — the pressure room 21 — alignment is carried out so that it may be arranged in each space. The case which does not illustrate the pressure room substrate 20 with which the nozzle plate 10 was stuck is made to complete installation and the ink jet type recording head 1.
[0058] (Example) While changing various ratios of the thickness of Pt layer [as opposed to the thickness of the whole lower electrode for the piezo electric crystal component by the manufacture approach of the above-mentioned operation gestalt 1] and manufacturing some, some piezo electric crystal components were manufactured as an example of a comparison also with ratios other than the ratio shown with the above-mentioned operation gestalt.
[0059] Drawing which measured the relation between the 100th page amount of preferred orientation and a piezoelectric constant d31 is shown about the piezo electric crystal component obtained as a result by drawing 8 . The piezoelectric constant d31 is especially measured in both high frequency (it measures using 14kHz and an ink jet head), and low frequency (it measures using DC actuation and a cantilever). In drawing 8 , when the 100th page amount of preferred orientation is small, it is shown that the 111st page amount of preferred orientation is large.
[0060] As shown in drawing 8 , although the piezo-electric multiplier d31 is so high that the 111st page amount of preferred orientation is high, when the 100th page amount of preferred orientation is 70% or less 40% or more, by low frequency actuation, it turns out that a suitable piezo-electric property is acquired by RF actuation which is used for an ink jet head. Moreover, that the piezo electric crystal component which shows such the amount of preferred orientation was manufactured was the case where the thickness of Pt layer to the thickness of the whole lower electrode was 30 - 50%.

[0061] In addition, it asked for measurement of a piezoelectric constant d31 from the variation rate at the time of electrical-potential-difference impression. Moreover, the "100th page amount of preferred orientation" said to this application means the ratio to the sum of I (100) of I (100), and I (110) and I (111), when diffraction reinforcement of the peak (2theta) corresponding to the XYZ side when using CuK alpha rays in an X diffraction wide angle method is set to I (XYZ).
[0062] (Other modifications) it not being based on the above-mentioned operation gestalt, but being able to deform and be adapted for versatility of this invention For example, the piezo electric crystal component manufactured by this invention can be adapted for manufacture of ferroelectric equipments, such as not only the piezo electric crystal component of the above-mentioned ink jet type recording head but a non-volatile semiconductor memory, a thin film capacitor, a pyroelectricity detector, a sensor, a surface-acoustic-waves optical waveguide, optical memory, a space optical modulator, a frequency doubler for diode lasers, etc., a dielectric device, pyroelectricity equipment, a piezoelectric device, and an electro-optic device.
[0063]
[Effect of the Invention] According to this invention, it is stabilized and the 100th page amount of preferred orientation of a piezo electric crystal thin film can be obtained with sufficient repeatability. As a result, the ratio of the 100th page amount of preferred orientation of a piezo electric crystal thin film and the 111st page amount of preferred orientation can be obtained with sufficient repeatability. The ink JIETO type recording head and printer list using the piezo electric crystal component and this which were equipped with the piezo-electric high property stabilized also in any of a RF and low frequency by this can be provided with the manufacture approach of a piezo electric crystal component.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] When this invention relates to the piezo electric crystal component which has an electric machine conversion function and is especially used for an ink jet type recording head, it relates to the manufacture approach of the piezo electric crystal component from which the outstanding piezo-electric property is acquired, an ink jet type recording head, a printer, and a piezo electric crystal component.

[Translation done.]

PRIOR ART

[Description of the Prior Art] A piezo electric crystal component is used for an ink jet type recording head as a driving source of the ink regurgitation of a printer. Generally this piezo electric crystal component is equipped with a piezo electric crystal thin film, the up electrode arranged on both sides of this, and a lower electrode, and is constituted.
[0003] The piezo electric crystal component which aimed at the property improvement is developed by specifying conventionally the crystal structure of the thin film which consists of PZT (PZT), or making Ti nucleus form on a lower electrode. For example, the PZT thin film which equipped JP,10-81016,A with the crystal structure of a rhombohedral system, and equipped it with the predetermined amount of preferred orientation is indicated. Moreover, the piezo electric crystal component in which the titanium nucleus was formed on the lower electrode of Ir is indicated by JP,8-335676,A.
[0004] However, with the conventional piezo electric crystal component, there was a problem that it was difficult to be stabilized and to obtain the predetermined amount of preferred orientation of a piezo electric crystal thin film with sufficient repeatability. It is difficult for such a piezo electric crystal component to acquire the stable piezo-electric high property, and it has become the factor which cannot fully obtain an ink jet type recording head or the printing engine performance of a printer.

EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, it is stabilized and the 100th page amount of preferred orientation of a piezo electric crystal thin film can be obtained with sufficient repeatability. As a result, the ratio of the 100th page amount of preferred orientation of a piezo electric crystal thin film and the 111st page amount of preferred orientation can be obtained with sufficient repeatability. The ink JIETO type recording head and printer list using the piezo electric crystal component and this which were equipped with the piezo-electric high property stabilized also in any of a RF and low frequency by this can be provided with the manufacture approach of a piezo electric crystal component.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The object of this invention is by canceling the above-mentioned trouble, being stabilized and obtaining the predetermined amount of preferred orientation of a piezo electric crystal thin film with sufficient repeatability to provide the ink JIETO type recording head using a piezo electric crystal component and this equipped with the stable piezo-electric high property, and a printer list with the manufacture approach of a piezo electric crystal component.

[Translation done.]

MEANS

[Means for Solving the Problem] The piezo electric crystal component of this invention is a piezo electric crystal component equipped with the lower electrode formed on ZrO2 film, the piezo electric crystal film formed on this lower electrode, and the up electrode formed on this piezo electric crystal film, and the 100th page amount of preferred orientation which measured said piezo electric crystal film by the X diffraction wide angle method is characterized by being 70% or less 40% or more.
[0007] Moreover, it is desirable that the 110th page amount of preferred orientation is 10% or less, and the 111st page amount of preferred orientation is the remainder.
[0008] the first pass which said especially lower electrode is located in ** maximum upper layer, and contains Ir, and the second layer which is located in the following layer and contains Pt — at least — having — and — this — to the thickness of the whole lower electrode, the thickness of the second layer is 50% or less, forms with a 4nm or more thickness [6nm or less] Ti layer on said lower electrode 30% or more, and forms the piezo electric crystal film on this Ti layer. **-1 [moreover,] — the third layer which is said layer [second] following layer, is located in the lowest layer of said lower electrode, and contains Ir — having — **** — **-2 — said second layer which contains Pt among said lower electrodes may be the lowest layer.
[0009] Moreover, said lower electrode is equipped with the first pass which is located in ** maximum upper layer and contains Pt, and the second layer which is located in the following layer and contains Ir at least. And it is characterized by for the thickness of this first pass being 40% or less, having formed the layer of with a 4nm or more thickness [6nm or less] Ti nucleus on said lower electrode 20% or more, to the thickness of the whole lower electrode, and forming the piezo electric crystal film on this Ti layer. **-1 [moreover,] — said second layer which contains Ir among said lower electrodes may be the lowest layer.
[0010] Moreover, this invention is an ink jet type recording head characterized by being prepared as an electrostrictive actuator on the diaphragm whose above-mentioned piezo electric crystal component is an installation side.
[0011] Moreover, this invention is a printer characterized by having this ink jet type recording head as a printing means.
[0012] Furthermore, the process at which this invention forms ZrO2 film on a substrate and the process which forms a lower electrode on this ZrO2 film, The process which forms the layer of with a 4nm or more thickness [6nm or less] Ti nucleus on this lower electrode, It is the manufacture approach of a piezo electric crystal component equipped with the process which forms the piezo electric crystal precursor film on this Ti layer, and a baking process. The ** aforementioned lower electrode It has at least the first pass which is located in the maximum upper layer and contains Ir, and the second layer which is located in the following layer and contains Pt. and — this — the process in which the thickness of the second layer is 50% or less, and forms said lower electrode 30% or more to the thickness of the whole lower electrode [whether it has at least the process which forms said second layer containing Pt, and the process which forms said first pass containing Ir on this second layer, and] Or the ** aforementioned lower electrode is equipped with the first pass which is located in the maximum upper layer and contains Pt, and the second layer which is located in the following layer and contains Ir at least.

And it is characterized by equipping the thickness of this first pass with the process which forms said second layer in which the process which is 40% or less and forms said lower electrode 20% or more to the thickness of the whole lower electrode contains Ir, and the process which forms said first pass containing Pt on this second layer at least.

[0013]

[Embodiment of the Invention] (Principle explanation) Drawing which measured the relation between the 100th page amount of preferred orientation of a piezo electric crystal thin film and the thickness of Ti nucleus is shown about the piezo electric crystal component which formed the lower electrode by which the laminating was carried out in the order of Ir layer / Pt layer / Ir layer, and Ti nucleus on ZrO2 film, formed the piezo electric crystal precursor film in drawing 9 further, and it was made to crystallize. In drawing 9 , the thickness of the second layer of the lower electrode with which sign (a) contains Pt shows about 10% of case to the thickness of the whole lower electrode. In this case, the thickness of Ti nucleus is able to raise the 100th page amount of preferred orientation to about 90% in 4nm or more 6nm or less. However, when it is going to adjust the 100th page amount of preferred orientation to a different value from this, it is too large, and fluctuation of the 100th page amount of preferred orientation to change of the thickness of Ti nucleus is stabilized, and cannot obtain the desired 100th page amount of preferred orientation with sufficient repeatability.

[0014] On the other hand, sign (b) of drawing 9 shows the case where the ratio to the thickness of the whole lower electrode of the thickness of the second layer of the lower electrode containing Pt is made to increase from the case of the above-mentioned (a). In this case, in response to the effect of Pt, the 111st page amount of preferred orientation of a piezo electric crystal thin film goes up, and while becoming lower than the case where the 100th page amount of preferred orientation is the above-mentioned (a), the value in which the thickness of Ti nucleus was stabilized by the 100th page amount of preferred orientation in 4nm or more 6nm or less is shown.

[0015] Thus, while setting thickness of Ti nucleus to 4-6nm, it becomes possible by adjusting the rate of the thickness of Pt layer to the thickness of the whole lower electrode to double with repeatability sufficient in proportion of a request of the 100th page amount of preferred orientation (ratio of the 100th page amount of preferred orientation and the 111st page amount of preferred orientation).

[0016] Hereafter, the gestalt of suitable operation of this invention is explained, referring to a drawing.

[0017] (Operation gestalt 1) Drawing 1 is layer structure section drawing which expanded the piezo electric crystal component part of the ink jet type recording head in this operation gestalt.

[0018] As shown in drawing 1 , on the oxide film 31, the piezo electric crystal component 40 carries out the laminating of ZrO2 film 32, the lower electrode 42, the piezo electric crystal thin film 43, and the up electrode 44 one by one, and is constituted.

[0019] An oxide film 31 is formed for example, on the pressure room substrate 20 which consists of single crystal silicon with a thickness of 220 micrometers. Suitably, the film which consists of silicon oxide (SiO2) is formed and obtained in thickness of 1.0 micrometers.

[0020] ZrO2 film 32 is a layer equipped with elasticity, and constitutes the diaphragm 30 united with an oxide film 31. In order to equip this ZrO2 film 32 with the function to give elasticity, it has 200nm or more thickness of 800nm or less preferably.

[0021] Between ZrO2 film 32 and the lower electrode 42, a metal which sticks both layers, and the adhesion layer (not shown) which consists of titanium or chromium preferably may be prepared. An adhesion layer is formed in order that the adhesion to the installation side of a piezo electric crystal component may improve, and when the adhesion concerned can be secured, it is not necessary to form it. Moreover, since when preparing an adhesion layer enables it to secure minimum adhesion, preferably considers as the thickness of 10nm or more.

[0022] The third layer, to 423 and the thickness of the lower electrode 42, it is 30% or more 50% or less of thickness, and the lower electrode 42 consists of 424 and the first passes 425 which are located in the maximum upper layer and contain Ir containing Pt for which are located in the lowest layer and Ir is included the second layer. Especially a limit does not have the thickness of the whole lower electrode 42, for example, it sets it to 100nm. In addition, it is desirable that the

relation of dT=3.6xd0+2.4xd1+0.8xd2+2.3xd3 is filled in the thickness of the adhesion layer before baking when the third layer of the thickness of the whole lower electrode after d3 and baking is set [the thickness of 423 / d1 and the thickness of the second layer] to dT for the thickness of d2 and the first pass, d0 and.

[0023] The layer (not shown) of Ti nucleus is formed on the lower electrode 42. Ti nucleus is 6nm or less in 4nm or more thickness.

[0024] The piezo electric crystal thin film 43 is the ferroelectric which consisted of crystals of usual piezoelectric ceramics, and consists of ferroelectricity piezoelectric ingredients, such as titanic-acid lead zirconate (PZT), and a thing which added metallic oxides, such as niobium oxide, nickel oxide, or a magnesium oxide, to this preferably. The presentation of the piezo electric crystal thin film 43 is suitably chosen in consideration of the property of a piezo electric crystal component, an application, etc. Specifically, lead titanate (PbTiO3), titanic-acid lead zirconate (Pb (Zr, Ti) O3), zirconic acid lead (PbZrO3), a lead titanate lanthanum (Pb, La) (TiO3), the PZT lanthanum (Pb, La) (Zr, Ti) (O3), or magnesium niobic acid zirconium lead titanate (Pb(Zr, Ti) (Mg, Nb) O3) is used suitably. Moreover, the film excellent in the piezo-electric property can be obtained by adding niobium (Nb) suitably in lead titanate or zirconic acid lead.

[0025] The 100th page amount of preferred orientation which measured the piezo electric crystal thin film 43 by the X diffraction wide angle method is 70% or less 40% or more. And the 111st page amount of preferred orientation of the 110th page amount of preferred orientation is the remainder 10% or less.

[0026] It is necessary to hold down the thickness of the piezo electric crystal thin film 43 to extent which a crack does not generate in a production process, and to make it thick to extent which presents sufficient displacement property on the other hand for example, and it is set to 1500nm.

[0027] The up electrode 44 is an electrode which becomes the lower electrode 42 and a pair, and is suitably constituted by Pt or Ir. The thickness of the up electrode 44 is about 50nm suitably.

[0028] Drawing 4 is the perspective view part sectional view showing the structure of the body of the ink jet type recording head of this invention.

[0029] As shown in drawing 4 , an ink jet type record head consists of a nozzle plate 10, a pressure room substrate 20, a diaphragm 30, and a piezo electric crystal component 40.

[0030] The pressure room substrate 20 is equipped with the pressure room (cavity) 21, the side attachment wall 22, the reservoir 23, and the feed hopper 24. The pressure room 21 is formed as space stored in order to carry out the regurgitation of the ink etc. by etching substrates, such as silicon. The side attachment wall 22 is formed so that the pressure room 21 may be divided. The reservoir 23 serves as passage for filling ink in each pressure room 21 in common. The feed hopper 24 is formed in each pressure room 21 possible [installation of ink] from the reservoir 23.

[0031] A nozzle plate 10 is stuck on one field of the pressure room substrate 20 so that the nozzle 11 may be arranged in the location corresponding to each of the pressure room 21 established in the pressure room substrate 20.

[0032] The laminating of an oxide film 31 and the ZrO2 film 32 is carried out, and a diaphragm 30 is formed, as mentioned above. The piezo electric crystal component 40 of this invention is formed as an electrostrictive actuator on the diaphragm 30 concerned. The piezo electric crystal component 40 equipped with the layer system shown in drawing 1 , respectively is formed in the location on the diaphragm 30 corresponding to each pressure room 21. The ink tank opening 35 is formed in a diaphragm 30, and supply to the pressure room substrate 20 interior of it is attained at it in the ink stored in the ink tank which is not illustrated.

[0033] The pressure room substrate 20 with which the nozzle plate 10 and the diaphragm 30 were formed is stored in the case which is not illustrated further, and constitutes the ink jet type recording head.

[0034] In the above-mentioned configuration, if an electrical potential difference is impressed between the lower electrode 42 of the piezo electric crystal component 40, and the up electrode 44 and the piezo electric crystal component 40 is distorted, a diaphragm 30 will deform corresponding to the distortion. A pressure is applied to the ink in the pressure room 21 according to the deformation, and the drop of ink carries out the regurgitation from a nozzle 11.

[0035] The perspective view which explains the structure of the printer 100 of this operation gestalt to drawing 5 is shown. As shown in drawing 5 , as for the printer 100, the ink jet type recording head 1, the tray 3, the exhaust port 4, the feed device 6, the control circuit 8, and control-panel 9 grade of this invention which is a printing means are prepared in the body 2 of a printer.
[0036] The tray 3 is constituted by the feed device 6 possible [supply] in the form 5 before printing. A control circuit 8 outputs the printing signal Sh which makes the feed signal Sd which makes a form 5 convey in the feed device 6, and printing perform to the ink jet type recording head 1 based on the printing information supplied from the control or the outside from a control panel 9. The feed device 6 consists of motor 600 grades which drive the rollers 601 and 602 and them which incorporate a form 5, and it is possible to incorporate a form 5 in a body 2 based on the feed signal Sd. If the ink jet type recording head 1 crosses the form 5 top supplied by the feed device 6, and is constituted movable and the printing signal Sh is supplied from a control circuit 8, when the piezo electric crystal component 40 deforms, it is possible to breathe out ink and to print on a form 5. The exhaust port 4 is the outlet which can discharge the form 5 which printing ended.
[0037] (Operation gestalt 2) Drawing 2 is layer structure section drawing which expanded the piezo electric crystal component part of the ink jet type recording head in the 2nd operation gestalt of this invention.
[0038] With this operation gestalt, the lower electrode 42 is 30% or more 50% or less of thickness to the thickness of the lower electrode 42, and the point which consists of 426 and the first passes (the maximum upper layer) 427 containing Ir containing Pt the second layer (the lowest layer) differs from the above-mentioned operation gestalt 1.
[0039] (Operation gestalt 3) Drawing 3 is layer structure section drawing which expanded the piezo electric crystal component part of the ink jet type recording head in the 3rd operation gestalt of this invention.
[0040] With this operation gestalt, to 428 and the thickness of the lower electrode 42, it is 20% or more 40% or less of thickness, and the second layer (the lowest layer) of the point which consists of the first passes (the maximum upper layer) 429 containing Pt for which the lower electrode 42 contains Ir differs from the above-mentioned operation gestalt 1.
[0041] (The manufacture approach) Next, the manufacture approach of the piezo electric crystal component of this invention is explained. Drawing 6 and drawing 7 are the cross sections showing the manufacture approach of the piezo electric crystal component of this invention, and an ink jet type recording head.
[0042] an oxide-film formation process (S1) — this process is a process which forms the oxide film 31 which carries out high temperature processing in the oxidizing atmosphere containing oxygen or a steam, and consists of oxidation silicon (SiO2). A CVD method besides the usually used oxidizing [thermally] method can also be used for this process.
[0043] It is the process which forms ZrO2 film 32 on the oxide film 31 on the process (S2) pressure room substrate 20 which forms ZrO2 film. This ZrO2 film 32 carries out high temperature processing of what formed the layer of Zr with the spatter or the vacuum deposition method in an oxygen ambient atmosphere, and is obtained.
[0044] If it is in the lower electrode concerning the process (S3) operation gestalt 1 which forms a lower electrode It consists of the process which contains Ir on ZrO2 film 32 and which forms 423 [layer / third], a process which is 30% or more 50% or less of thickness to the thickness of the lower electrode 42 on this third layer, and contains Pt and which forms 424 [layer / second], and a process which forms the first pass 425 containing Ir on this second layer.
[0045] If it is in the lower electrode concerning the operation gestalt 2, on ZrO2 film 32, to the thickness of the lower electrode 42, it is 30% or more 50% or less of thickness, and consists of a process containing Pt which forms 426 [layer / second], and a process which forms the first pass 424 containing Ir on this second layer.
[0046] If it is in the lower electrode concerning the operation gestalt 3, it consists of a process which contains Ir on ZrO2 film 32 and which forms 428 [layer / second], and a process which forms the first pass 429 which is 20% or more 40% or less of thickness, and contains Pt to the thickness of the lower electrode 42 on this second layer.

[0047] On ZrO2 film 32, each class 423–429 makes Ir or Pt adhere in a spatter etc., and forms it, respectively. In addition, in advance of formation of the lower electrode 42, the adhesion layer (not shown) which consists of titanium or chromium may be formed with a spatter or a vacuum deposition method.
[0048] This process is a process which forms a titanium crystal (not shown) in the shape of an island on the lower electrode 42 by a spatter etc. like ** which forms Ti nucleus (layer). By growing up PZT by using a titanium crystal as a nucleus, crystal growth happens from a lower electrode side, and forming Ti nucleus (layer) has it, and it is because a column–like crystal is obtained.
[precise]
[0049] the process (S4) which forms the piezo electric crystal precursor film — this process is a process which forms piezo electric crystal precursor film 43' with a sol–gel method.
[0050] First, the sol which consists of an organic metal alkoxide solution is applied on Ti nucleus by the applying methods, such as a spin coat. Subsequently, fixed time amount desiccation is carried out with constant temperature, and a solvent is evaporated. After desiccation, fixed time amount cleaning is further carried out at a predetermined elevated temperature under an atmospheric–air ambient atmosphere, and the pyrolysis of the organic ligand configurated to the metal is carried out, and it considers as a metallic oxide. Each process of this spreading, desiccation, and cleaning is repeated 4 times or more the number of predetermined times, for example, and the laminating of the piezo electric crystal precursor film of four or more layers is carried out. By these desiccation and cleaning processings, the metal alkoxide and acetate in a solution form the network of a metal, oxygen, and a metal through the pyrolysis of a ligand.
[0051] It is the process which it calcinates [process] and crystallizes the piezo electric crystal precursor film after formation of baking process (S5) piezo electric crystal precursor film 43'. By this baking, piezo electric crystal precursor film 43' changes to the thin film in which the perovskite crystal structure is formed in from the precursor of an amorphous condition, and an electric machine conversion operation is shown, and the 100th page amount of preferred orientation measured by the X diffraction wide angle method serves as 70% or less of piezo electric crystal thin film 40% or more.
[0052] The up electrode 44 is formed by electron beam vacuum deposition or the spatter on the piezo electric crystal thin film 43 at the up electrode formation process (S6) last.
[0053] If it etches and operates orthopedically in the configuration of having been suitable for the activity part and the piezoelectric component 40 obtained at the above process is manufactured possible [impression of an electrical potential difference] to vertical inter–electrode one, it is possible to make it operate as a piezo electric crystal component of this invention.
[0054] The obtained piezoelectric component 40 is etched so that an ink jet type recording head may be suited, and it is explained below about the process fabricated in the configuration as a piezo electric crystal component based on drawing 7 .
[0055] a piezo electric crystal component forming cycle (S7) — the mask of the piezo electric crystal component 40 is first carried out to the configuration fitted to each pressure room 21, and the perimeter is etched. Specifically, the resist ingredient of uniform thickness is first applied on an up electrode using approaches, such as the spinner method and a spray method. Subsequently, after forming a mask in the configuration of a piezo electric crystal component, exposure and development of are done, and a resist pattern is formed on the up electrode 44. Ion milling or the dry etching method usually used for this is applied, etching clearance of the up electrode 44, the piezo electric crystal thin film 43, and the lower electrode 42 is carried out, and each piezo electric crystal component 40 is fabricated.
[0056] Anisotropic etching which used activity gases, such as anisotropic etching or parallel plate mold reactive ion etching, is performed to the field of another side of a pressure room formation process (S8), next the pressure room substrate 20 with which the piezo electric crystal component 40 was formed, and the pressure room 21 is formed in it. The part left behind without being etched becomes a side attachment wall 22.
[0057] A nozzle plate 10 is stuck on the pressure room substrate 20 after etching with adhesives at the nozzle plate lamination process (S9) last. the time of lamination — each nozzle 11 — the pressure room 21 — alignment is carried out so that it may be arranged in each space. The case

which does not illustrate the pressure room substrate 20 with which the nozzle plate 10 was stuck is made to complete installation and the ink jet type recording head 1.

[Translation done.]

EXAMPLE

(Example) While changing various ratios of the thickness of Pt layer [as opposed to the thickness of the whole lower electrode for the piezo electric crystal component by the manufacture approach of the above-mentioned operation gestalt 1] and manufacturing some, some piezo electric crystal components were manufactured as an example of a comparison also with ratios other than the ratio shown with the above-mentioned operation gestalt.
[0059] Drawing which measured the relation between the 100th page amount of preferred orientation and a piezoelectric constant d31 is shown about the piezo electric crystal component obtained as a result by drawing 8 . The piezoelectric constant d31 is especially measured in both high frequency (it measures using 14kHz and an ink jet head), and low frequency (it measures using DC actuation and a cantilever). In drawing 8 , when the 100th page amount of preferred orientation is small, it is shown that the 111st page amount of preferred orientation is large.
[0060] As shown in drawing 8 , although the piezo-electric multiplier d31 is so high that the 111st page amount of preferred orientation is high, when the 100th page amount of preferred orientation is 70% or less 40% or more, by low frequency actuation, it turns out that a suitable piezo-electric property is acquired by RF actuation which is used for an ink jet head. Moreover, that the piezo electric crystal component which shows such the amount of preferred orientation was manufactured was the case where the thickness of Pt layer to the thickness of the whole lower electrode was 30 - 50%.
[0061] In addition, it asked for measurement of a piezoelectric constant d31 from the variation rate at the time of electrical-potential-difference impression. Moreover, the "100th page amount of preferred orientation" said to this application means the ratio to the sum of I (100) of I (100), and I (110) and I (111), when diffraction reinforcement of the peak (2theta) corresponding to the XYZ side when using CuK alpha rays in an X diffraction wide angle method is set to I (XYZ).
[0062] (Other modifications) it not being based on the above-mentioned operation gestalt, but being able to deform and be adapted for versatility of this invention For example, the piezo electric crystal component manufactured by this invention can be adapted for manufacture of ferroelectric equipments, such as not only the piezo electric crystal component of the above-mentioned ink jet type recording head but a non-volatile semiconductor memory, a thin film capacitor, a pyroelectricity detector, a sensor, a surface-acoustic-waves optical waveguide, optical memory, a space optical modulator, a frequency doubler for diode lasers, etc., a dielectric device, pyroelectricity equipment, a piezoelectric device, and an electro-optic device.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The sectional view of the piezo electric crystal component of the operation gestalt 1
[Drawing 2] The sectional view of the piezo electric crystal component of the operation gestalt 2
[Drawing 3] The sectional view of the piezo electric crystal component of the operation gestalt 3
[Drawing 4] The perspective view part sectional view showing the structure of the body of an ink jet type recording head
[Drawing 5] The perspective view showing the structure of the printer which used the ink jet type recording head of this invention
[Drawing 6] The cross section showing the manufacture approach of the ink jet type recording head of this invention
[Drawing 7] The cross section showing the manufacture approach of the ink jet type recording head of this invention
[Drawing 8] Drawing showing the relation between the 100th page amount of preferred orientation and a piezoelectric constant d31
[Drawing 9] Drawing showing the relation between the 100th page amount of preferred orientation and the thickness of Ti nucleus
[Description of Notations]
20 Pressure Room Substrate
30 Diaphragm
31 Oxide Film
32 ZrO2 Film
40 Piezo Electric Crystal Component
42 Lower Electrode
423 Third Layer (Ir)
424 Second Layer (Pt)
425 First Pass (Ir)
426 Second Layer (Pt)
427 First Pass (Ir)
428 Second Layer (Ir)
429 First Pass (Pt)
43 Piezo Electric Crystal Thin Film
44 Up Electrode

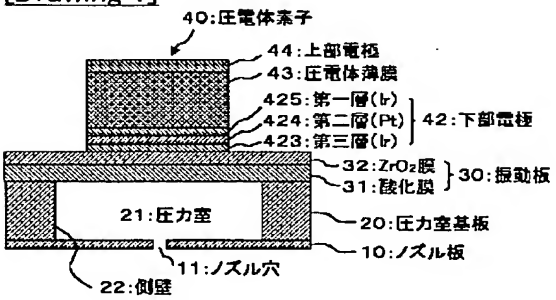
[Translation done.]

* NOTICES *

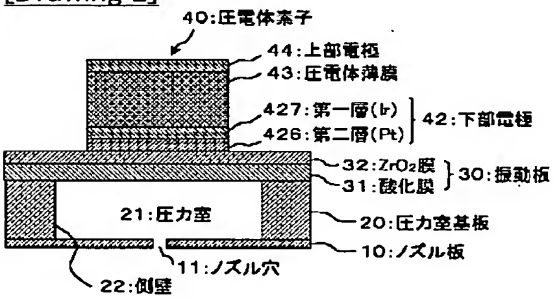
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

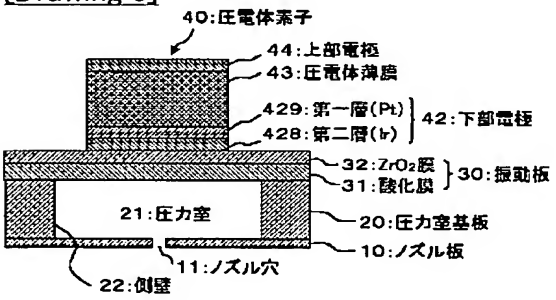
[Drawing 1]



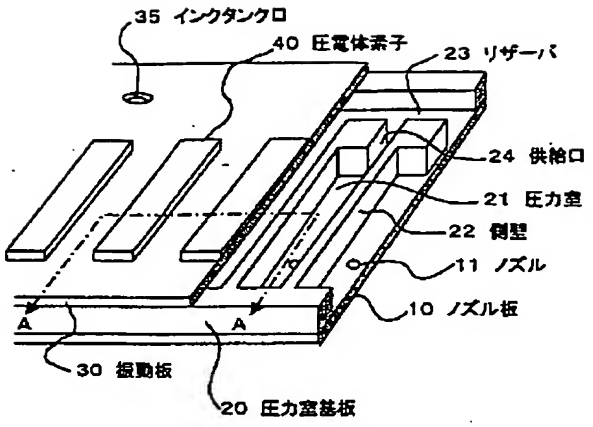
[Drawing 2]



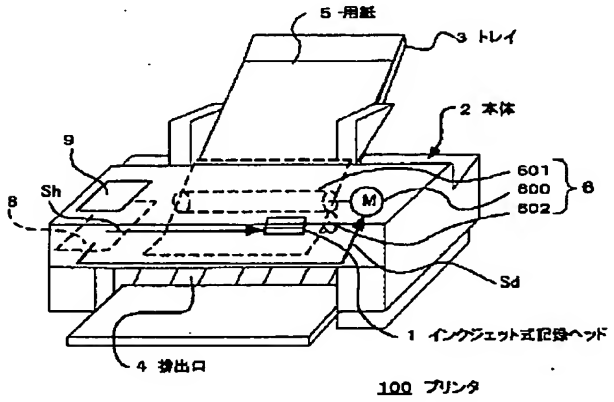
[Drawing 3]



[Drawing 4]

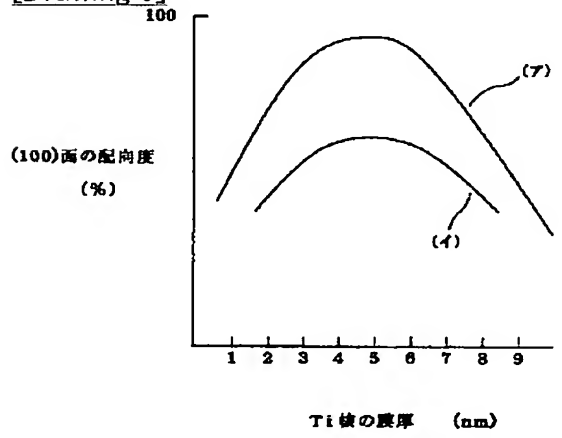


[Drawing 5]

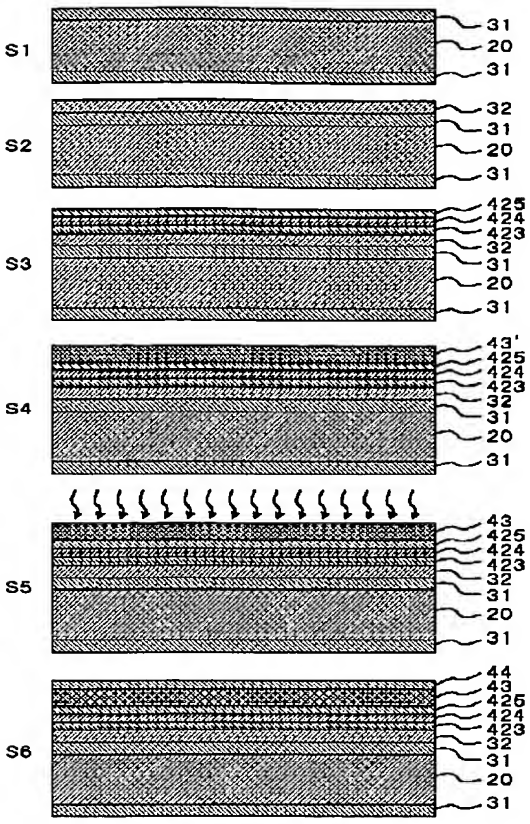


100 プリンタ

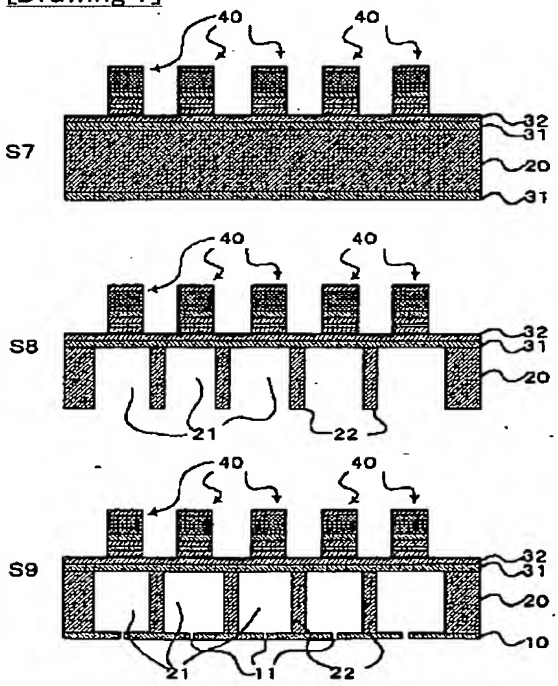
[Drawing 9]



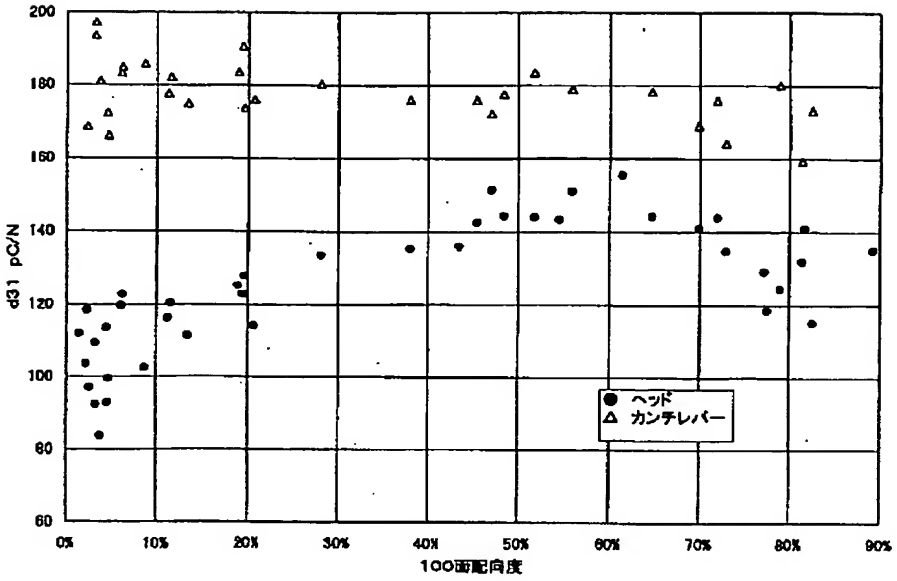
[Drawing 6]



[Drawing 7]



[Drawing 8]



[Translation done.]

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2/16			１０３Ｈ	
Ｈ０１Ｌ　41/18		Ｈ０１Ｌ　41/08	Ｕ	

審査請求　未請求　請求項の数11　ＯＬ　（全９頁）　最終頁に続く

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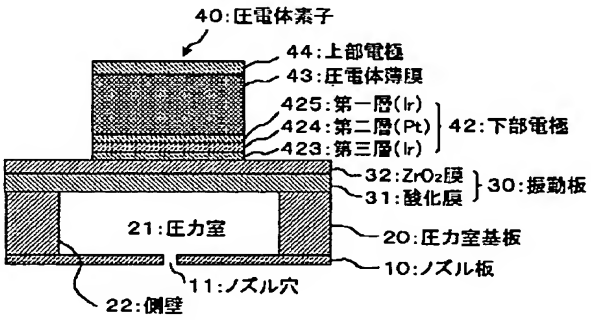
(54)【発明の名称】　圧電体素子、インクジェット式記録ヘッド、プリンタ、及び圧電体素子の製造方法

(57)【要約】
【課題】　安定した高い圧電特性を備えた圧電体素子およびこれを用いたインクジェット式記録ヘッド、プリンタを提供する。
【解決手段】　ZrO_2膜３２上に、下部電極４２（Ｉｒを含む第三層４２３、Ｐｔを含む第二層４２４、Ｉｒを含む第一層４２５）、４ｎｍ以上６ｎｍ以下のＴｉ層、圧電体薄膜４３、および上部電極４４、を順次積層してなり、Ｘ線回折広角法により測定した圧電体膜４３の１００面配向度が４０％以上７０％以下、１１０面配向度が１０％以下、１１１面配向度が残部である。この場合、下部電極第二層４２４の厚さが下部電極４２全体の厚さに対して３０％以上５０％以下である。



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【特許請求の範囲】

【請求項１】　ZrO_2膜上に形成された下部電極と、該下部電極上に形成された圧電体膜と、該圧電体膜上に形成された上部電極とを備えた圧電体素子であって、
前記圧電体膜は、Ｘ線回折広角法により測定した１００面配向度が４０％以上７０％以下であることを特徴とする圧電体素子。

【請求項２】　請求項１に記載の圧電体素子であって、
前記圧電体膜は、Ｘ線回折広角法により測定した１１０面配向度が１０％以下、１１１面配向度が残部であることを特徴とする圧電体素子。

【請求項３】　請求項１に記載の圧電体素子であって、
前記下部電極は、最上層に位置しＩｒを含む第一層と、次層に位置しＰｔを含む第二層とを少なくとも備え、かつ、該第二層の厚さが下部電極全体の厚さに対して３０％以上５０％以下であり、
前記下部電極上に厚さ４ｎｍ以上６ｎｍ以下のＴｉ層を形成し、該Ｔｉ層上に圧電体膜を形成したことを特徴とする圧電体素子。

【請求項４】　請求項３に記載の圧電体素子であって、
前記下部電極は、前記第二層の次層であって前記下部電極の最下層に位置し且つＩｒを含む第三層を備えたことを特徴とする圧電体素子。

【請求項５】　請求項３に記載の圧電体素子であって、
前記下部電極のうち、Ｐｔを含む前記第二層が最下層であることを特徴とする圧電体素子。

【請求項６】　請求項１に記載の圧電体素子であって、
前記下部電極は、最上層に位置しＰｔを含む第一層と、次層に位置しＩｒを含む第二層とを少なくとも備え、かつ、該第一層の厚さが下部電極全体の厚さに対して２０％以上４０％以下であり、
前記下部電極上に厚さ４ｎｍ以上６ｎｍ以下のＴｉ層を形成し、該Ｔｉ層上に圧電体膜を形成したことを特徴とする圧電体素子。

【請求項７】　請求項６に記載の圧電体素子であって、
前記下部電極のうち、Ｉｒを含む前記第二層が最下層であることを特徴とする圧電体素子。

【請求項８】　請求項１ないし請求項７のいずれかに記載の圧電体素子が、該圧電体素子の設置面である振動板上に圧電アクチュエータとして設けられていることを特徴とするインクジェット式記録ヘッド。

【請求項９】　請求項８に記載のインクジェット式記録ヘッドを印字手段として備えていることを特徴とするプリンタ。

【請求項１０】　基板上に、ZrO_2膜を形成する工程と、
該ZrO_2膜上に下部電極を形成する工程と、
該下部電極上に厚さ４ｎｍ以上６ｎｍ以下のＴｉ層を形成する工程と、
該Ｔｉ層上に圧電体前駆体膜を形成する工程と、

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焼成工程と、を備える圧電体素子の製造方法であって、
前記下部電極は、最上層に位置しＩｒを含む第一層と、次層に位置しＰｔを含む第二層とを少なくとも備え、かつ、該第二層の厚さが下部電極全体の厚さに対して３０％以上５０％以下であり、
前記下部電極を形成する工程は、
Ｐｔを含む前記第二層を形成する工程と、
該第二層上にＩｒを含む前記第一層を形成する工程とを少なくとも備える、ことを特徴とする圧電体素子の製造方法。

【請求項１１】　基板上に、ZrO_2膜を形成する工程と、
該ZrO_2膜上に下部電極を形成する工程と、
該下部電極上に厚さ４ｎｍ以上６ｎｍ以下のＴｉ層を形成する工程と、
該Ｔｉ層上に圧電体前駆体膜を形成する工程と、
焼成工程と、を備える圧電体素子の製造方法であって、
前記下部電極は、最上層に位置しＰｔを含む第一層と、次層に位置しＩｒを含む第二層とを少なくとも備え、かつ、該第一層の厚さが下部電極全体の厚さに対して２０％以上４０％以下であり、
前記下部電極を形成する工程は、
Ｉｒを含む前記第二層を形成する工程と、
該第二層上にＰｔを含む前記第一層を形成する工程とを少なくとも備える、ことを特徴とする圧電体素子の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、電気機械変換機能を有する圧電体素子に係り、特に、インクジェット式記録ヘッドに用いた際に、優れた圧電特性が得られる圧電体素子、インクジェット式記録ヘッド、プリンタおよび圧電体素子の製造方法に関する。

【０００２】

【従来の技術】インクジェット式記録ヘッドは、プリンタのインク吐出の駆動源として圧電体素子を用いる。この圧電体素子は、一般的に、圧電体薄膜とこれを挟んで配置される上部電極および下部電極とを備えて構成される。

【０００３】従来、ジルコン酸チタン酸鉛（ＰＺＴ）からなる薄膜の結晶構造を規定したり、下部電極上にＴｉ核を形成させることにより、特性改善を図った圧電体素子が開発されている。たとえば、特開平１０－８１０１６号公報には、菱面体晶系の結晶構造を備えかつ所定の配向度を備えたＰＺＴ薄膜が開示されている。また、特開平８－３３５６７６号公報には、Ｉｒの下部電極上にチタン核を形成した圧電体素子が開示されている。

【０００４】しかし、従来の圧電体素子では、圧電体薄膜の所定の配向度を安定して再現性良く得ることが困難であるという問題があった。このような圧電体素子は、

安定した高い圧電特性を得ることが難しく、インクジェット式記録ヘッドないしはプリンタの印字性能を十分に得られない要因となっている。

【０００５】

【発明が解決しようとする課題】本発明の目的は、上記問題点を解消して、圧電体薄膜の所定の配向度を安定して再現性良く得ることにより、安定した高い圧電特性を備えた圧電体素子およびこれを用いたインクジェット式記録ヘッド、プリンタ並びに圧電体素子の製造方法を提供することにある。

【０００６】

【課題を解決するための手段】本発明の圧電体素子は、ZrO_2膜上に形成された下部電極と、該下部電極上に形成された圧電体膜と、該圧電体膜上に形成された上部電極とを備えた圧電体素子であって、前記圧電体膜は、Ｘ線回折広角法により測定した１００面配向度が４０％以上７０％以下であることを特徴とする。

【０００７】また、１１０面配向度が１０％以下、１１１面配向度が残部であることが好ましい。

【０００８】特に、前記下部電極は、

①最上層に位置しＩｒを含む第一層と、次層に位置しＰｔを含む第二層とを少なくとも備え、かつ、該第二層の厚さが下部電極全体の厚さに対して３０％以上５０％以下であり、前記下部電極上に厚さ４ｎｍ以上６ｎｍ以下のＴｉ層を形成し、該Ｔｉ層上に圧電体膜を形成したものである。また、

①－１前記第二層の次層であって前記下部電極の最下層に位置し且つＩｒを含む第三層を備えていてもよく、

①－２前記下部電極のうち、Ｐｔを含む前記第二層が最下層であってもよい。

【０００９】また、前記下部電極は、

②最上層に位置しＰｔを含む第一層と、次層に位置しＩｒを含む第二層とを少なくとも備え、かつ、該第一層の厚さが下部電極全体の厚さに対して２０％以上４０％以下であり、前記下部電極上に厚さ４ｎｍ以上６ｎｍ以下のＴｉ核の層を形成し、該Ｔｉ層上に圧電体膜を形成したことを特徴とするものである。また、

②－１前記下部電極のうち、Ｉｒを含む前記第二層が最下層であってもよい。

【００１０】また、本発明は、上記した圧電体素子が設置面である振動板上に圧電アクチュエータとして設けられていることを特徴とするインクジェット式記録ヘッドである。

【００１１】また、本発明は、このインクジェット式記録ヘッドを印字手段として備えていることを特徴とするプリンタである。

【００１２】さらに、本発明は、基板上に、ZrO_2膜を形成する工程と、該ZrO_2膜上に下部電極を形成する工程と、該下部電極上に厚さ４ｎｍ以上６ｎｍ以下のＴｉ核の層を形成する工程と、該Ｔｉ層上に圧電体前駆体膜を形成する工程と、焼成工程と、を備える圧電体素子の製造方法であって、

①前記下部電極は、最上層に位置しＩｒを含む第一層と、次層に位置しＰｔを含む第二層とを少なくとも備え、かつ、該第二層の厚さが下部電極全体の厚さに対して３０％以上５０％以下であり、前記下部電極を形成する工程は、Ｐｔを含む前記第二層を形成する工程と、該第二層上にＩｒを含む前記第一層を形成する工程とを少なくとも備えるか、または、

②前記下部電極は、最上層に位置しＰｔを含む第一層と、次層に位置しＩｒを含む第二層とを少なくとも備え、かつ、該第一層の厚さが下部電極全体の厚さに対して２０％以上４０％以下であり、前記下部電極を形成する工程は、Ｉｒを含む前記第二層を形成する工程と、該第二層上にＰｔを含む前記第一層を形成する工程とを少なくとも備えることを特徴とするものである。

【００１３】

【発明の実施の形態】（原理説明）図９に、ZrO_2膜上にＩｒ層／Ｐｔ層／Ｉｒ層の順で積層された下部電極と、Ｔｉ核とを形成し、更に圧電体前駆体膜を形成して結晶化させた圧電体素子について、圧電体薄膜の１００面配向度とＴｉ核の厚さとの関係を測定した図を示す。図９において、符号（ア）は、Ｐｔを含む下部電極第二層の厚さが下部電極全体の厚さに対して１０％程度の場合を示す。この場合には、Ｔｉ核の厚さが４ｎｍ以上６ｎｍ以下では１００面配向度を約９０％まで高めることが可能である。しかし、１００面配向度をこれと異なる値に調整しようとする場合、Ｔｉ核の厚さの変化に対する１００面配向度の変動が大きすぎ、所望の１００面配向度を安定して再現性良く得ることができない。

【００１４】これに対して図９の符号（イ）は、Ｐｔを含む下部電極第二層の厚さの下部電極全体の厚さに対する比率を上記（ア）の場合より増加させた場合を示す。この場合には、Ｐｔの影響を受けて圧電体薄膜の１１１面配向度が上昇し、１００面配向度が上記（ア）の場合より低くなるとともに、Ｔｉ核の厚さが４ｎｍ以上６ｎｍ以下において、１００面配向度が安定した値を示している。

【００１５】このように、Ｔｉ核の厚さを４～６ｎｍとするとともに、下部電極全体の厚さに対するＰｔ層の厚さの割合を調節することにより、１００面配向度（１００面配向度と１１１面配向度との比率）を所望の割合に再現性良く合わせ込むことが可能となる。

【００１６】以下、本発明の好適な実施の形態を、図面を参照しながら説明する。

【００１７】（実施形態１）図１は、本実施形態におけるインクジェット式記録ヘッドの圧電体素子部分を拡大した層構造断面図である。

【００１８】図１に示すように、圧電体素子４０は、酸化膜３１上にZrO_2膜３２、下部電極４２、圧電体薄

膜４３および上部電極４４を順次積層して構成されている。

【００１９】酸化膜３１は、例えば厚さ２２０μｍの単結晶シリコンからなる圧力室基板２０上に形成する。好適には、酸化ケイ素（SiO_2）からなる膜を１．０μｍの厚さに形成して得る。

【００２０】ZrO_2膜３２は、弾性を備える層であって、酸化膜３１と一体となって振動板３０を構成している。このZrO_2膜３２は、弾性を与える機能を備えるため、好ましくは、２００ｎｍ以上８００ｎｍ以下の厚みを有する。

【００２１】ZrO_2膜３２と下部電極４２の間には、双方の層を密着するような金属、好ましくは、チタンまたはクロムからなる密着層（図示しない）を設けてもよい。密着層は、圧電体素子の設置面への密着性が良くするために形成するものであり、当該密着性が確保できる場合には形成しなくてもよい。また、密着層を設ける場合は、最低限の密着性が確保できるようにするため、好ましくは、１０ｎｍ以上の厚みとする。

【００２２】下部電極４２は、最下層に位置しＩｒを含む第三層４２３と、下部電極４２の厚さに対して３０％以上５０％以下の厚さであって、Ｐｔを含む第二層４２４と、最上層に位置しＩｒを含む第一層４２５とから構成されている。下部電極４２の全体の厚みは特に制限はなく、例えば１００ｎｍとする。なお、焼成前における密着層の厚みをｄ０、第三層４２３の厚みをｄ１、第二層の厚みをｄ２、第一層の厚みをｄ３、焼成後の下部電極全体の厚みをｄＴとしたとき、ｄＴ＝３．６×ｄ０＋２．４×ｄ１＋０．８×ｄ２＋２．３×ｄ３の関係が満たされることが好ましい。

【００２３】下部電極４２の上にはＴｉ核の層（図示しない）が形成されている。Ｔｉ核は、４ｎｍ以上６ｎｍ以下の厚みである。

【００２４】圧電体薄膜４３は、通常の圧電性セラミックスの結晶で構成された強誘電体であり、好ましくは、チタン酸ジルコン酸鉛（ＰＺＴ）等の強誘電性圧電性材料や、これに酸化ニオブ、酸化ニッケルまたは酸化マグネシウム等の金属酸化物を添加したものからなる。圧電体薄膜４３の組成は圧電体素子の特性、用途等を考慮して適宜選択する。具体的には、チタン酸鉛（$PbTiO_3$）、チタン酸ジルコン酸鉛（$Pb(Zr,Ti)O_3$）、ジルコニウム酸鉛（$PbZrO_3$）、チタン酸鉛ランタン（$(Pb,La),TiO_3$）、ジルコン酸チタン酸鉛ランタン（$(Pb,La)(Zr,Ti)O_3$）又は、マグネシウムニオブ酸ジルコニウムチタン酸鉛（$Pb(Zr,Ti)(Mg,Nb)O_3$）等が好適に用いられる。また、チタン酸鉛やジルコニウム酸鉛にニオブ（Ｎｂ）を適宜添加することにより、圧電特性に優れた膜を得ることができる。

【００２５】圧電体薄膜４３は、Ｘ線回折広角法により測定した１００面配向度が４０％以上７０％以下である。そして、１１０面配向度は１０％以下、１１１面配向度が残部である。

【００２６】圧電体薄膜４３の厚みは、製造工程でクラックが発生しない程度に抑え、一方、十分な変位特性を呈する程度に厚くする必要があり、例えば１５００ｎｍとする。

【００２７】上部電極４４は、下部電極４２と対になる電極であり、好適には、ＰｔまたはＩｒにより構成される。上部電極４４の厚みは、好適には５０ｎｍ程度である。

【００２８】図４は、本発明のインクジェット式記録ヘッドの主要部の構造を示す斜視図一部断面図である。

【００２９】図４に示すように、インクジェット式記録ヘッドは、ノズル板１０、圧力室基板２０、振動板３０および圧電体素子４０から構成される。

【００３０】圧力室基板２０は、圧力室（キャビティ）２１、側壁２２、リザーバ２３および供給口２４を備えている。圧力室２１は、シリコン等の基板をエッチングすることにより、インクなどを吐出するために貯蔵する空間として形成されたものである。側壁２２は、圧力室２１を仕切るよう形成されている。リザーバ２３は、インクを共通して各圧力室２１に充たすための流路となっている。供給口２４は、リザーバ２３から各圧力室２１へインクを導入可能に形成されている。

【００３１】ノズル板１０は、圧力室基板２０に設けられた圧力室２１の各々に対応する位置にそのノズル１１が配置されるよう、圧力室基板２０の一方の面に貼り合わせられている。

【００３２】振動板３０は、上述したように酸化膜３１とZrO_2膜３２とを積層して形成されたものである。本発明の圧電体素子４０は、当該振動板３０の上に圧電アクチュエータとして設けられている。各圧力室２１に対応する振動板３０上の位置には、それぞれ図１に示す層構造を備えた圧電体素子４０が設けられている。振動板３０には、インクタンクロ３５が設けられて、図示しないインクタンクに貯蔵されているインクを圧力室基板２０内部に供給可能になっている。

【００３３】ノズル板１０および振動板３０が設けられた圧力室基板２０は、さらに図示しない筐体に収められてインクジェット式記録ヘッドを構成している。

【００３４】上記構成において、圧電体素子４０の下部電極４２と上部電極４４との間に電圧が印加されて圧電体素子４０が歪むとその歪みに対応して振動板３０が変形する。その変形により圧力室２１内のインクに圧力が加えられ、ノズル１１からインクの液滴が吐出するようになっている。

【００３５】図５に本実施形態のプリンタ１００の構造を説明する斜視図を示す。図５に示すように、プリンタ１００は、プリンタ本体２に、印字手段である本発明の

インクジェット式記録ヘッド１、トレイ３、排出口４、給紙機構６、制御回路８および操作パネル９等が設けられている。

【００３６】トレイ３は、印字前の用紙５を給紙機構６に供給可能に構成されている。制御回路８は、操作パネル９からの制御または外部から供給される印字情報に基いて、用紙５の搬送を給紙機構６に行わせる給紙信号Ｓｄや印字をインクジェット式記録ヘッド１に行わせる印字信号Ｓｈを出力するようになっている。給紙機構６は、用紙５を取り込むローラ６０１と６０２およびそれらを駆動するモータ６００等で構成され、給紙信号Ｓｄに基いて用紙５を本体２内に取り込むことが可能になっている。インクジェット式記録ヘッド１は、給紙機構６により供給された用紙５の上を横切って移動可能に構成され、制御回路８から印字信号Ｓｈが供給されると、圧電体素子４０が変形することによりインクが吐出され用紙５上に印字することが可能になっている。排出口４は、印字が終了した用紙５を排出可能な出口となっている。

【００３７】（実施形態２）図２は、本発明の第２の実施形態におけるインクジェット式記録ヘッドの圧電体素子部分を拡大した層構造断面図である。

【００３８】本実施形態では、下部電極４２は、下部電極４２の厚さに対して３０％以上５０％以下の厚さであって、Ｐｔを含む第二層（最下層）４２６と、Ｉｒを含む第一層（最上層）４２７とから構成されている点が、上記実施形態１と異なっている。

【００３９】（実施形態３）図３は、本発明の第３の実施形態におけるインクジェット式記録ヘッドの圧電体素子部分を拡大した層構造断面図である。

【００４０】本実施形態では、下部電極４２は、Ｉｒを含む第二層（最下層）４２８と、下部電極４２の厚さに対して２０％以上４０％以下の厚さであって、Ｐｔを含む第一層（最上層）４２９とから構成されている点が、上記実施形態１と異なっている。

【００４１】（製造方法）次に、本発明の圧電体素子の製造方法を説明する。図６及び図７は、本発明の圧電体素子及びインクジェット式記録ヘッドの製造方法を示す断面模式図である。

【００４２】酸化膜形成工程（Ｓ１）

この工程は、酸素或いは水蒸気を含む酸化性雰囲気中で高温処理し、酸化珪素（ＳｉＯ２）からなる酸化膜３１を形成する工程である。この工程には通常用いる熱酸化法の他、ＣＶＤ法を使用することもできる。

【００４３】ＺｒＯ２膜を形成する工程（Ｓ２）

圧力室基板２０上の酸化膜３１の上に、ＺｒＯ２膜３２を形成する工程である。このＺｒＯ２膜３２は、スパッタ法または真空蒸着法等によりＺｒの層を形成したものを酸素雰囲気中で高温処理して得られる。

【００４４】下部電極を形成する工程（Ｓ３）

実施形態１に係る下部電極にあっては、ＺｒＯ２膜３２上に、Ｉｒを含む第三層４２３を形成する工程と、該第三層上に、下部電極４２の厚さに対して３０％以上５０％以下の厚さであって、Ｐｔを含む第二層４２４を形成する工程と、該第二層上にＩｒを含む第一層４２５を形成する工程とからなる。

【００４５】実施形態２に係る下部電極にあっては、ＺｒＯ２膜３２上に、下部電極４２の厚さに対して３０％以上５０％以下の厚さであって、Ｐｔを含む第二層４２６を形成する工程と、該第二層上に、Ｉｒを含む第一層４２４を形成する工程とからなる。

【００４６】実施形態３に係る下部電極にあっては、ＺｒＯ２膜３２上に、Ｉｒを含む第二層４２８を形成する工程と、該第二層上に、下部電極４２の厚さに対して２０％以上４０％以下の厚さであって、Ｐｔを含む第一層４２９を形成する工程とからなる。

【００４７】各層４２３～４２９は、それぞれＩｒまたはＰｔをＺｒＯ２膜３２上に、スパッタ法等で付着させて形成する。なお、下部電極４２の形成に先立ち、チタン又はクロムからなる密着層（図示せず）をスパッタ法又は真空蒸着法により形成しても良い。

【００４８】Ｔｉ核（層）を形成する工程

この工程は、スパッタ法等により、下部電極４２上にチタン結晶（図示せず）を島状に形成する工程である。Ｔｉ核（層）を形成するのは、チタン結晶を核としてＰＺＴを成長させることにより、結晶成長が下部電極側から起こり、緻密で柱状の結晶が得られるからである。

【００４９】圧電体前駆体膜を形成する工程（Ｓ４）

この工程は、ゾル・ゲル法により、圧電体前駆体膜４３’を形成する工程である。

【００５０】まず、有機金属アルコキシド溶液からなるゾルをスピンコート等の塗布法によりＴｉ核上に塗布する。次いで、一定温度で一定時間乾燥させ、溶媒を蒸発させる。乾燥後、さらに大気雰囲気下において所定の高温で一定時間脱脂し、金属に配位している有機の配位子を熱分解させ、金属酸化物とする。この塗布、乾燥、脱脂の各工程を所定回数、例えば４回以上繰り返して４層以上の圧電体前駆体膜を積層する。これらの乾燥と脱脂処理により、溶液中の金属アルコキシドと酢酸塩とは配位子の熱分解を経て金属、酸素、金属のネットワークを形成する。

【００５１】焼成工程（Ｓ５）

圧電体前駆体膜４３’の形成後、焼成して、圧電体前駆体膜を結晶化させる工程である。この焼成により、圧電体前駆体膜４３’は、アモルファス状態の前駆体からペロブスカイト結晶構造が形成され、電気機械変換作用を示す薄膜に変化し、Ｘ線回折広角法により測定した１００面配向度が４０％以上７０％以下の圧電体薄膜となる。

【００５２】上部電極形成工程（Ｓ６）

最後に、圧電体薄膜４３上に、電子ビーム蒸着法またはスパッタ法により上部電極４４を形成する。

【００５３】以上の工程で得られた、圧電性素子４０を、使用箇所に適した形状にエッチングして整形し上下電極間に電圧を印加可能に製造すれば、本発明の圧電体素子として動作させることが可能である。

【００５４】得られた圧電性素子４０を、インクジェット式記録ヘッドに適合するようにエッチングして、圧電体素子としての形状に成形する工程について、図７に基いて、以下に説明する。

【００５５】圧電体素子成形工程（Ｓ７）

まず、圧電体素子４０を、各圧力室２１に適合させた形状にマスクし、その周囲をエッチングする。具体的には、まずスピンナー法、スプレー法等の方法を用いて均一な厚さのレジスト材料を上部電極上に塗布する。次いで、マスクを圧電体素子の形状に形成してから露光・現像して、レジストパターンを上部電極４４上に形成する。これに通常用いるイオンミリングまたはドライエッチング法等を適用して、上部電極４４、圧電体薄膜４３、下部電極４２をエッチング除去し、各圧電体素子４０を成形する。

【００５６】圧力室形成工程（Ｓ８）

次に、圧電体素子４０が形成された圧力室基板２０の他方の面に、異方性エッチングまたは平行平板型反応性イオンエッチング等の活性気体を用いた異方性エッチングを施し、圧力室２１を形成する。エッチングされずに残された部分が側壁２２になる。

【００５７】ノズル板貼り合わせ工程（Ｓ９）最後に、エッチング後の圧力室基板２０にノズル板１０を接着剤で貼り合わせる。貼り合わせのときに各ノズル１１が圧力室２１各々の空間に配置されるよう位置合わせする。ノズル板１０が貼り合わせられた圧力室基板２０を図示しない筐体に取り付け、インクジェット式記録ヘッド１を完成させる。

【００５８】（実施例）上記実施形態１の製造方法による圧電体素子を、下部電極全体の厚さに対するＰｔ層の厚さの比率を種々変えて幾つか製造するとともに、比較例として、上記実施形態で示した比率以外の比率によっても圧電体素子を幾つか製造した。

【００５９】図８に、その結果得られた圧電体素子について、１００面配向度と圧電定数ｄ３１との関係を測定した図を示す。特に圧電定数ｄ３１は、高周波（１４ｋＨｚ、インクジェットヘッドを用いて測定）および低周波（ＤＣ駆動、カンチレバーを用いて測定）の両者において測定している。図８において、１００面配向度が小さいときは、１１１面配向度が大きいことを示している。

【００６０】図８に示されるように、低周波駆動では１１１面配向度が高いほど圧電乗数ｄ３１が高いが、インクジェットヘッドに使用されるような高周波駆動では、

１００面配向度が４０％以上７０％以下のときに、好適な圧電特性が得られることがわかる。また、このような配向度を示す圧電体素子が製造されたのは、下部電極全体の厚さに対するＰｔ層の厚さが３０～５０％の場合であった。

【００６１】なお、圧電定数ｄ３１の測定は、電圧印加時の変位から求めた。また、本願にいう「１００面配向度」とは、Ｘ線回折広角法においてＣｕＫα線を用いたときのＸＹＺ面に対応するピーク（２θ）の回折強度をＩ（ＸＹＺ）としたとき、Ｉ（１００）のＩ（１００）とＩ（１１０）とＩ（１１１）との和に対する比率を意味する。

【００６２】（その他の変形例）本発明は、上記実施形態によらず種々に変形して適応することが可能である。例えば、本発明で製造した圧電体素子は上記インクジェット式記録ヘッドの圧電体素子のみならず、不揮発性半導体記憶装置、薄膜コンデンサ、パイロ電気検出器、センサ、表面弾性波光学導波管、光学記憶装置、空間光変調器、ダイオードレーザ用周波数二倍器等のような強誘電体装置、誘電体装置、パイロ電気装置、圧電装置、および電気光学装置の製造に適応することができる。

【００６３】

【発明の効果】本発明によれば、圧電体薄膜の１００面配向度を安定して再現性良く得ることができる。ひいては、圧電体薄膜の１００面配向度と１１１面配向度との比率を再現性良く得ることができる。これにより、高周波および低周波のいずれにおいても安定した高い圧電特性を備えた圧電体素子およびこれを用いたインクジェット式記録ヘッド、プリンタ並びに圧電体素子の製造方法を提供することができる。

【図面の簡単な説明】

【図１】　実施形態１の圧電体素子の断面図

【図２】　実施形態２の圧電体素子の断面図

【図３】　実施形態３の圧電体素子の断面図

【図４】　インクジェット式記録ヘッドの主要部の構造を示す斜視図一部断面図

【図５】　本発明のインクジェット式記録ヘッドを使用したプリンタの構造を示す斜視図

【図６】　本発明のインクジェット式記録ヘッドの製造方法を示す断面模式図

【図７】　本発明のインクジェット式記録ヘッドの製造方法を示す断面模式図

【図８】　１００面配向度と圧電定数ｄ３１との関係を示す図

【図９】　１００面配向度とＴｉ核の厚さとの関係を示す図

【符号の説明】

２０　　圧力室基板

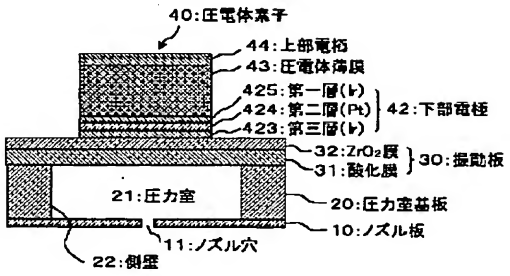
３０　　振動板

３１　　酸化膜

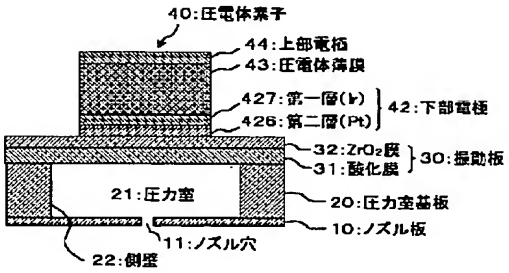
３２　　ZrO_2 膜
４０　　圧電体素子
４２　　下部電極
４２３　第三層（Ｉｒ）
４２４　第二層（Ｐｔ）
４２５　第一層（Ｉｒ）

４２６　第二層（Ｐｔ）
４２７　第一層（Ｉｒ）
４２８　第二層（Ｉｒ）
４２９　第一層（Ｐｔ）
４３　　圧電体薄膜
４４　　上部電極

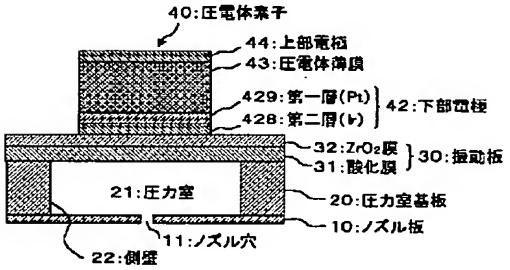
【図１】



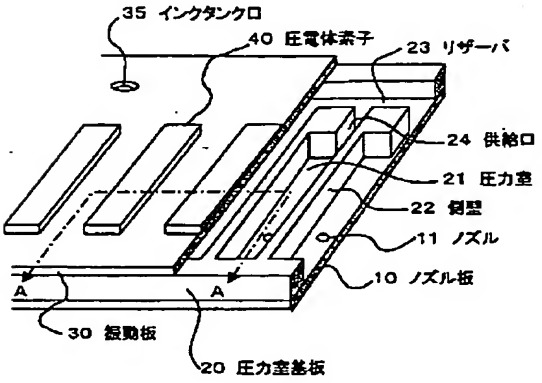
【図２】



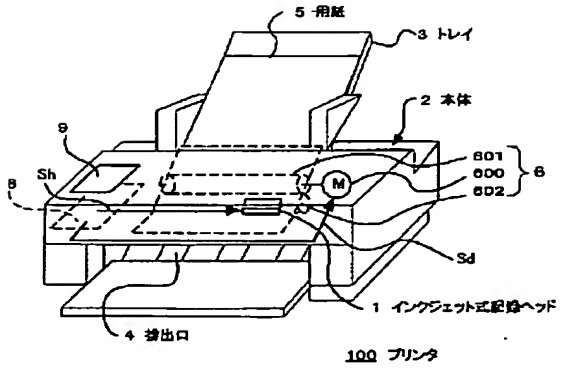
【図３】



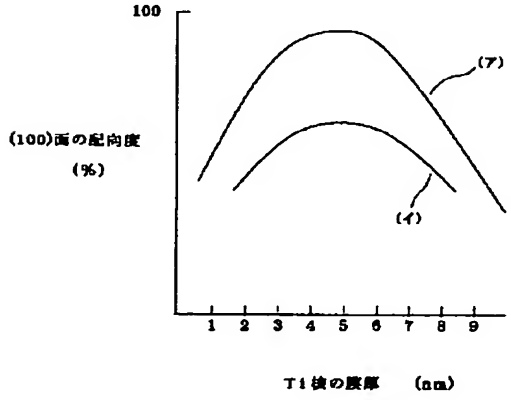
【図４】



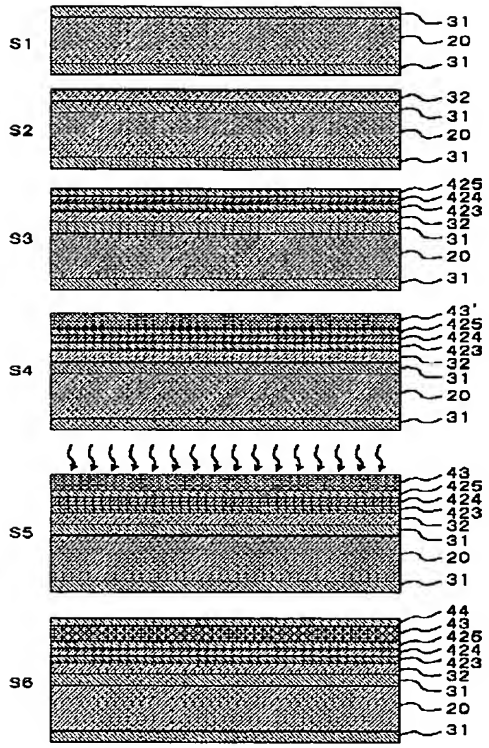
【図５】



【図９】



【図６】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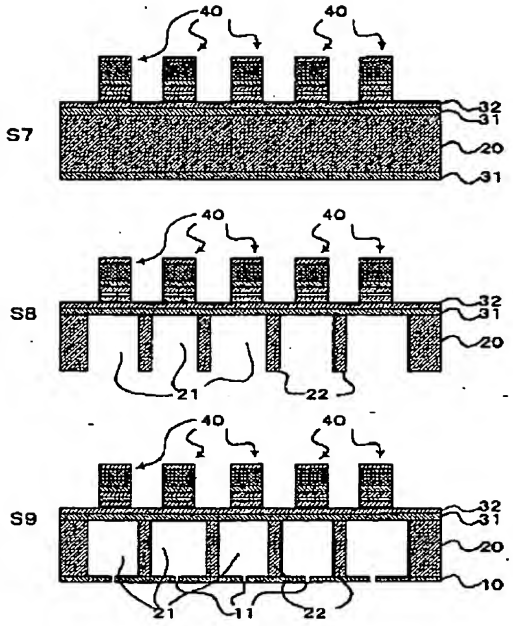
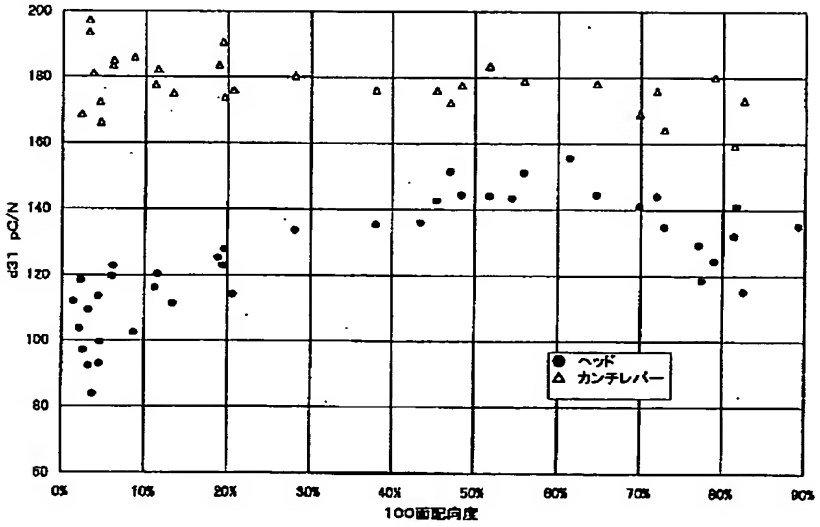
31

【図７】


S7
40
40
32
31
20
31
S8
40
40
32
31
20
21
22
S9
40
40
32
31
20
10
21
11
22

【図８】


d31 pC/N
200
180
160
140
120
100
80
60
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100面配向度
● ヘッド
△ カンチレバー

フロントページの続き

(51)Int.Cl.[7]	識別記号	F I		テーマコード(参考)
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